Osmotic coefficients

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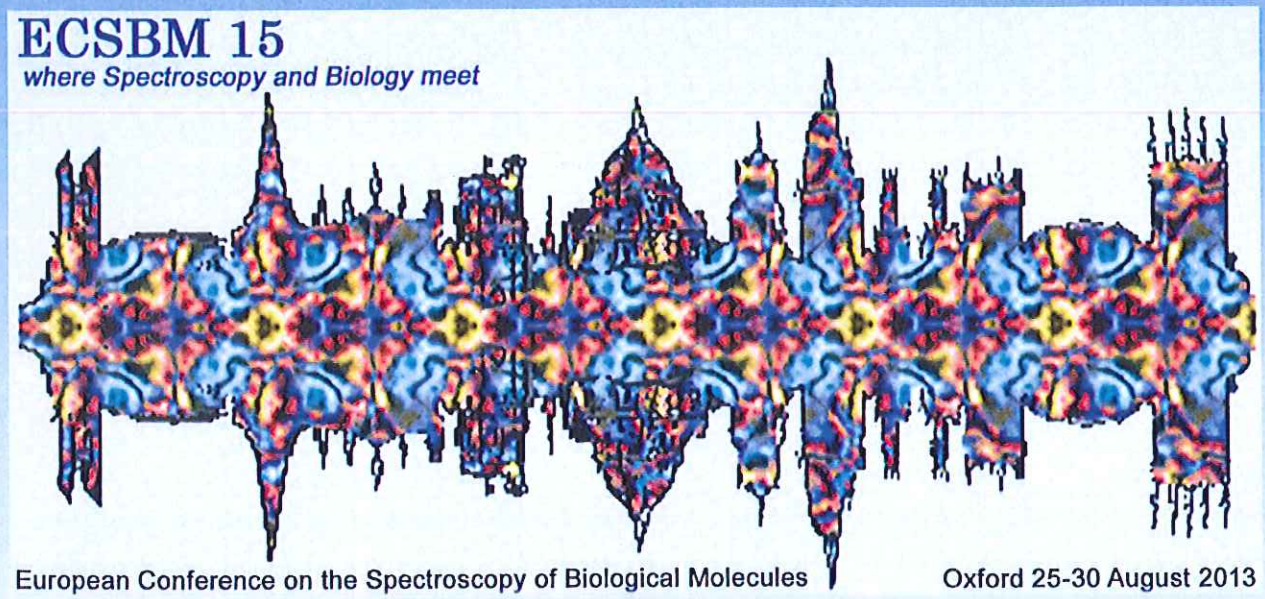

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OSMOTIC COEFFICIENTS

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To preserve the overall shape of living cells the osmolarity/osmolality plays an important role.[1] The osmolarity of the extracellular fluid is usually due to small inorganic ions from dissociated strong electrolytes. [1] In a paper by Niels Bjerrum at the 16th Scandinavian Scientist Meeting in 1916, he concluded that the van't Hoff factor had erroneously been considered as a measure of the degree of dissociation of strong electrolytes. [2] Bjerrum proposed the strong electrolytes to be completely dissociated and he introduced an osmotic coefficient to account for the measured osmotic pressure.[2] The molal osmotic coefficient, φ, was expressed by Robinson and Stokes in terms of water activity, defined as the vapour pressure of an aqueous solution relative to that of pure water. [3] We proposed the osmotic coefficient to be a product of two factors, $\varphi = \varphi^d \varphi^w$. [4] The term φ^d depends on the degree of dissociation of the dissolved strong electrolyte (NaCl, NH_4Cl, Na_2SO_4 or $(NH_4)_2SO_4$) and φ^w depends on changes in hydrogen bonded water clusters with solute concentration. [4] The φ^w-term was measured from intensity changes of a band at 180 cm^{-1} in the $R(\bar{\nu})$ -representation of the Raman spectrum. [4] This contribution presents results for aqueous solution of KCl and $MgCl_2$.

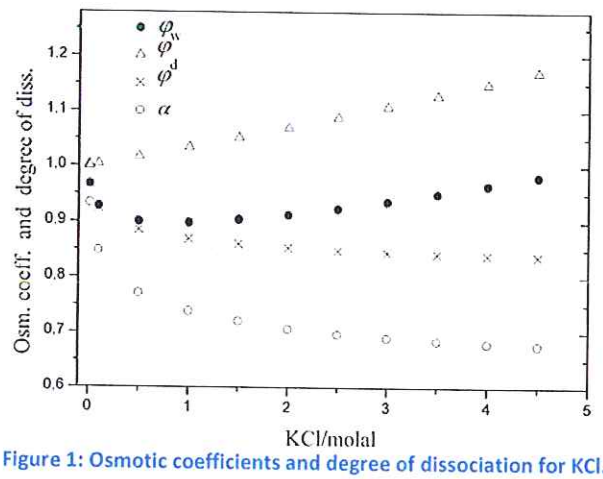

Figure 1: Osmotic coefficients and degree of dissociation for KCl.

Raman spectra were recorded as previously described. [4] For KCl the area of the 180 cm^{-1} band was used to calculate the amount of tetrahedral bound water. The ratio between the amount of "free" water in pure water relative to that in a solution defines φ^w. Subsequently φ^d was calculated from values of the osmotic coefficient, φ, given by Hamer and Wu. [5] See results in Figure 1. The minimum in φ around 0.5 molal is caused by a combination of changes in water structure, φ^w, and electrolyte dissociation, φ^d. At high concentration the degree of dissociation, α, approaches 0.65, thus KCl is not completely dissociated. Similar results were obtained for $MgCl_2$ solutions, where also the strong H_2O----Mg^{2+} binding was taken into account. We hope the results will lead to a better understanding of osmolarity/osmolality on a molecular scale.

References

[1] B. Alberts, A. Johnson, J. Lewis, M. Raff, K. Roberts, P. Walter, *Molecular Biology of the Cell 2008*, 5th ed., Garland Science, New York, US and Abingdon, UK, pp. 663-664
[2] N. Bjerrum, *Fysisk Tidsskrift 1916-1917*, **15**, 59-73: Translated to English in *Niels Bjerrum, Selected Papers*, eds. N. Bohr *et al.*, Munksgaard, Copenhagen, Denmark, 1949 pp. 58-70.
[3] R.A. Robinson, R.H. Stokes, *Electrolyte Solutions 1959*, 2nd ed., Butterworth, London, UK, pp. 25 and 29.
[4] M. Frosch, M. Bilde. O.F. Nielsen, *J. Phys. Chem. A 2010*, **114**, pp. 11933-11942.
[5] W.J. Hamer, Y.-C. Wu, *J. Phys. Chem. Ref. Data 1972*, **1**, 1047-1099.